AN022

Combustion Module-CRDS for $\delta^{13}C$ analysis of imported honey and detection of adulteration.

A fast screening method of imported honey to test for product adulteration with high fructose corn syrup.

Keywords:

Material: Honey, high-fructose corn syrup
Process: Stable isotopes, $\delta^{13}C$, CM-CRDS

Summary and Relevance:

Natural products may have divergent stable isotope compositions based on a variety of factors. These stable isotopic compositions create a measurable isotopic signature for a certain botanical class. Carbon isotope ratio analysis is a well-known tool used to detect food adulteration by comparing botanical isotopic signatures. The stable carbon isotope value, $\delta^{13}C$, is very sensitive to plant type. Scientists have not used this value to its full extent to detect food adulteration due to the considerable difficulty, time and cost of obtaining $\delta^{13}C$ data using traditional IRMS instrumentation.

In contrast, Picarro's Combustion Module-Cavity Ring-Down Spectroscopy (CM-CRDS) platform can quickly test for fraudulent adulteration of honey by measuring the $^{13}C/^{12}C$ isotope ratio of analyzed samples. Honey is a high-value product that can easily be adulterated with High Fructose Corn Syrup (HFCS), a far cheaper ingredient. Other high value candidates for CM-CRDS testing include vanillin, bioplastics, and maple syrup. Plants presenting C3 and C4 photosynthetic pathways show distinctly different $^{13}C/^{12}C$ ratios[1]. For that reason, natural products from corn and other C4 plants can be easily distinguished from natural products of C3 nectar-bearing

plants used by bees for honey production. By leveraging this inherent isotope ratio differential, Picarro's CM-CRDS platform has demonstrated its ability to detect adulterations of pure honey at addition levels of 5%, 10% and 15% by weight. The precision of the isotopic analyses achieved by the Picarro CM-CRDS system is comparable to analyses achieved with EA-IRMS-based testing routines. The accuracy of the isotopically measured adulteration value was always within < 0.1‰ of the weighed composition, even at the 5% adulteration level.

Picarro's table-top CM-CRDS system can replace a far larger and more costly EA-IRMS system and doesn't require a skilled lab technician for operation. Up to 147 samples of honey can be analyzed in one automated sequence with no human intervention over the course of 24 hours. Unlike EA-IRMS analyzers, Picarro CM-CRDS analyzers require extremely infrequent calibration. This stability translates into higher throughput and better utilization. The automation capabilities and ease-of-use can save significant man-hours in a lab setting. This feature set and reliability can translate into annualized cost savings of 50% or greater, including instrument depreciation, labor, and consumables.

In this application note we present isotopic carbon analysis data of various samples of imported honey. Additionally, we mixed pure honey with known amounts of HFCS to create an adulteration curve and test the analytical capabilities of the CM-CRDS system. A Combustion Module (CM) front-end converted the carbon in honey samples into CO_2 which was then automatically passed to Picarro's CRDS detector for high-precision carbon isotope measurement.

Process:

Ten different imported honey samples were sourced from a honey importer for analysis and comparison with IRMS measurements. In addition, a pure honey product was mixed in various proportions with high fructose corn syrup to simulate adulteration cases. The resultant CO_2 from combustion is collected via a high throughput interface. After an appropriate mixing time to ensure isotopic equilibration, this CO_2 automatically passed into the CRDS sampling chamber. The isotopic signature was then recorded during an 8-minute acquisition period.

Results:

Photosynthetic carbon isotope fractionation is related to carbon dioxide uptake and enzymatic processes[2]. The so-called C3 plants, named due to the number of carbons in an intermediate molecule in the relevant biochemical pathway, discriminate more heavily against ^{13}C than the C4 plants and therefore have more negative $\delta^{13}C$ values. So, as expected, the data shows a dramatic difference in sampled $\delta^{13}C$ values between the pure honey from C3 plants and samples adulterated with HFCS derived from corn, a C4 type plant (see Figure 1).

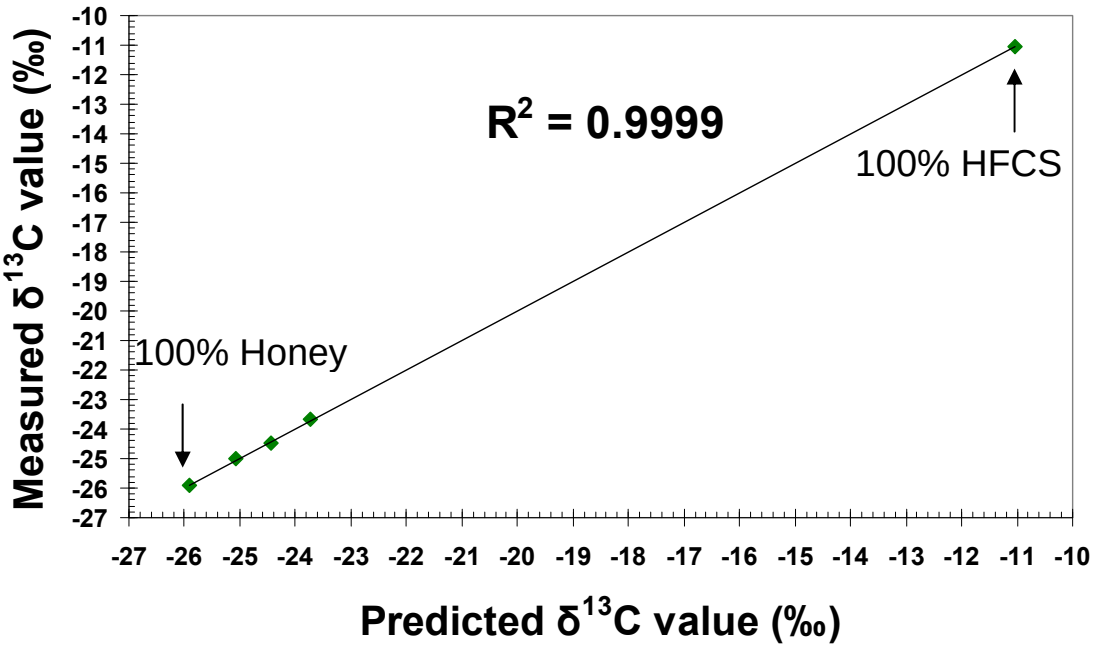

Figure 1: Honey adulterated with corn syrup at 5%, 10% & 15% w/w
Exceptional correlation of measured versus calculated $\delta^{13}C$ values:
$\Delta\delta$ values are < 0.1 ‰, even at the 5% adulteration level

Second, even the ten pure honey samples from C3 plants show distinct isotopic ratios, indicating clear differentials based on point-of origin. Importantly, this new method produces absolute values that are in agreement with IRMS data. Finally, the Picarro instrument's excellent precision is confirmed with standard deviations between 0.032‰ and 0.184‰.

Table 1 below documents the comparison between the Picarro data and the IRMS results. The correlation provides validation that this time-based optical technique is clearly capable of rivaling IRMS for these applications.

Sample	CRDS $\delta^{13}C$ (‰)	S.D. (‰)	IRMS $\delta^{13}C$ (‰)	$\Delta\delta$ (‰)
Honey A	-22.22	0.165	-22.2	-0.02
Honey B	-21.85	0.120	-22.0	0.15
Honey C	-25.22	0.184	-25.6	0.38
Honey D	-25.08	0.047	-25.1	0.02
Honey E	-27.20	0.082	-26.8	-0.40
Honey F	-24.47	0.089	-24.4	-0.07
Honey G	-23.77	0.032	-23.9	0.13
Honey H	-23.65	0.065	-23.9	0.15
Honey I	-23.66	0.046	-23.8	0.14
Honey J	-23.74	0.107	-24.2	0.46

Once again, the excellent correlation and the superb precision of the results (see column 5) are indicative of the strengths of this instrument.

Comments:

A new generation of CRDS-based analyzers enables simple and fast measurement of stable isotope ratios of carbon, oxygen and hydrogen. This study confirms that $\delta^{13}C$ values derived from these instruments can be used as a fast screening tool for edible oil adulteration: to determine whether higher value oils have been diluted with corn-derived oil.

References:

1. Carbon Isotope Analyses in Food Technology, Harold W. Krueger*, Richard H. Reesman, Mass Spectrometry Reviews, Vol. 1, Issue 3, Pages 205 - 236
2. Carbon Isotope Discrimination and Photosynthesis, G D Farquhar et al, Annual Review of Plant Physiology and Plant Molecular Biolog, Vol. 40: 503-537 (1989)